Article

Experimental and Theoretical Study of the Kinetics of Dissociation in *cis*-[RuCl₂(P-P)(N-N)] Type Complexes

Marcos C. R. Monteiro,[a] Fabio B. Nascimento,[b] Eliana M. A. Valle,[b] Javier Ellena,[c] Eduardo E. Castellano,[c] Alzir A. Batista[b] and Sergio de Paula Machado[,a]*

[a]*Instituto de Química, Universidade Federal do Rio de Janeiro,*
21941-590 Rio de Janeiro-RJ, Brazil

[b]*Departamento de Química, Universidade Federal de São Carlos, CP 676,*
13565-905 São Carlos-SP, Brazil

[c]*Instituto de Física de São Carlos, Universidade de São Paulo, CP 369,*
13560-970 São Carlos-SP, Brazil

As reações de substituição [RuCl₂(P-P)(N-N)] + L → [RuCl(L)(P-P)(N-N)]⁺ + Cl⁻, onde P-P = 1,4-bis(difenilfosfino)butano e N-N = 2,2´-bipiridina, 4,4´-dimetóxi-2,2´-bipiridina, 4,4´-dimetil-2,2´-bipiridina e 4,4´-dicloro-2,2´-bipiridina, L = piridina (py) ou 4-metilpiridina (4-pic), foram estudadas sob condições de pseudo-primeira ordem. As reações ocorrem por um mecanismo dissociativo e as constantes de velocidade nas reações de substituição aumentam com o aumento do pKₐ dos ligantes N-heterocíclicos e com a diminuição dos potenciais de oxidação do centro metálico. Quanto mais alta é a porcentagem de participação dos orbitais atômicos d do metal na formação do HOMO, conforme calculado pelo método DFT, mais fácil é a dissociação do cloreto da esfera de coordenação do complexo. Nos espectros de ³¹P{¹H} RMN da série de complexos de fórmula geral [RuCl(L)(P-P)(N-N)]PF₆, há dois dubletos com Δσ < 1, o que é consistente com produtos formados pela dissociação do cloreto *trans* ao átomo de fósforo nos precursores.

The substitution reactions [RuCl₂(P-P)(N-N)] + L → [RuCl(L)(P-P)(N-N)]⁺ + Cl⁻, where P-P = 1,4-bis(diphenylphosphino)butane and N-N = 2,2´-bipyridine, 4,4´-dimethoxy-2,2´-bipyridine, 4,4´-dimethylpyridine-2,2´-bipyridine and 4,4´-dichloro-2,2´-bipyridine, L = pyridine (py) or 4-methylpyridine (4-pic), were studied under pseudo-first order conditions. The reactions proceeded by means of a dissociative mechanism. The rate constants of the substitution reactions increased as the pKₐ of the N-heterocyclic ligands increased and as the oxidation potential of the metal center decreased. The greater the participation of the atomic d orbitals of the metal in the HOMO, according to DFT calculations, the easier is the dissociation of the chloride from the coordination sphere of the complex. In the ³¹P{¹H} NMR spectra of the series of complexes of general formula [RuCl(L)(P-P)(N-N)]PF₆, there are two doublets with Δσ < 1. This is consistent with products formed by dissociation of the chloride *trans* to one of the phosphorus atoms in the precursors.

Keywords: DFT, ruthenium complexes, *trans*-effect, kinetics, dissociation

Introduction

A phenomenon in which one ligand labilizes another *trans* to itself is known as the "*trans* effect".[1] According to the classical theory, this effect is strong when the metal is coordinated to π-acids, which are able to form bonds by back donation, accepting electron density from the metal

*e-mail: sergiopm@iq.ufrj.br

center. In this case, the *trans* effect probably takes place because the π-acids generate a pathway for the removal of electron density from the vicinity of the *trans* ligands, thereby stabilizing the transition state and facilitating nucleophilic attack on the metal center.

A rich coordination and organometallic chemistry of ruthenium has developed in recent years, and reports on the reactivity and catalytic applications of ruthenium complexes containing tertiary phosphine ligands are of particular interest.[2-6] In this context, a study of the kinetics

of dissociation of one chloride from *cis*-[RuCl$_2$(P-P)(N-N)] complexes, where P-P = 1,4-bis(diphenylphosphino)butane and N-N = 2,2´-bipyridine, 4,4´-dimethoxy-2,2´-bipyridine, 4,4´-dimethylpyridine-2,2´-bipyridine and 4,4´-dichloro-2,2´-bipyridine, was undertaken. It is well known that, in six-coordinated complexes, ligand substitution reactions usually proceed by means of a dissociative mechanism. Thus, one ligand has to be dissociated to create a vacancy that will promptly be occupied by other ligand, including coordinating solvent molecules. In this process, the electronic and steric properties of the ligands can play a crucial role.

Quantum chemical calculations, especially by the DFT method, have turned out to be a valuable instrument for describing the molecular properties of diverse transition metal coordination compounds. Over the last few years, we have used the DFT method for this purpose.[7-11] This paper describes the use of this method as an aid to the investigation of the possible influence of the diphosphine and X-bipy ligands on the rate of dissociation of one chloride from the precursors, leading to the corresponding [RuCl(L)(P-P)(N-N)]$^+$ complexes. Differential pulse voltammetry was used to track the kinetics of the reactions. The DFT calculations were then employed with the objective of supporting the interpretation of the experimental rate constants found for the reactions.

Although the kinetic measurements and DFT calculations were conducted only with the ligands pyridine and 4-methylpyridine, any other pyridine derivative could be used with the same precursors to give similar results, since the controlling process is dissociative. In addition to the kinetic experiments and the theoretical calculations, the X-ray structure of [RuCl(4-vinylpyridine)(P-P)(bipy)]PF$_6$ is reported here.

The goals of this research were to determine the experimental kinetic data for the chloride dissociation in the *cis*-[RuCl$_2$(P-P)(N-N)] series and to analyze how these data correlate with the results of DFT calculations.
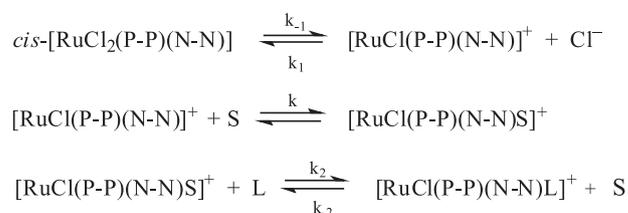
Experimental

Chemicals

Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. RuCl$_3$3H$_2$O, 1,4-bis(diphenylphosphino)butane (dppb), 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (Me-bipy), 4,4´-dimethoxy-2,2´-bipyridine (MeO-bipy), 4,4´-dichloro-2,2´-bipyridine (Cl-bipy), 4-vinylpyridine (4-vnpy) and 4-phenylpyridine (4-Phpy) were used as received from Aldrich. The *cis*-[RuCl$_2$(dppb)(N-N)] complexes were prepared by procedures published elsewhere.[12-16]

Instrumentation

The NMR experiments were performed at 293 K on a Bruker 9.4 T spectrometer. The ^{31}P{^{1}H} NMR spectra were recorded in dichloromethane solutions at 161.98 MHz with H$_3$PO$_4$ (85%) as external reference. Differential pulse voltammetry experiments (used for the kinetics measurements) were carried out with a Bioanalytical Systems BAS-100B/W electrochemical analyzer in dichloromethane containing 0.10 mol L^{-1} Bu$_4$NClO$_4$ (tbap) (Fluka Purum) as electrolyte. The working and auxiliary electrodes were stationary Pt foils; a Lugging capillary probe was used and the reference electrode was Ag/AgCl. Under these conditions, ferrocene is oxidized at 0.43 V (Fc$^+$/Fc). Cyclic voltammetry was used to measure the oxidation potentials of the complexes; the experimental conditions were the same as those employed for pulse voltammetry.

Substitution reactions were performed under pseudo-first order conditions (excess of the entering ligand L). The kinetic data were analyzed in terms of the system[17,18]

$$cis\text{-}[RuCl_2(P\text{-}P)(N\text{-}N)] \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [RuCl(P\text{-}P)(N\text{-}N)]^+ + Cl^-$$

$$[RuCl(P\text{-}P)(N\text{-}N)]^+ + S \overset{k}{\rightleftharpoons} [RuCl(P\text{-}P)(N\text{-}N)S]^+$$

$$[RuCl(P\text{-}P)(N\text{-}N)S]^+ + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [RuCl(P\text{-}P)(N\text{-}N)L]^+ + S$$

where S (solvent) is CH$_2$Cl$_2$, and the equation:

$$k_{obs} = \frac{k_2 k_{-1}[L] + k_1 k_{-2}[Cl^-]}{k_1[Cl^-] + k_2[L]}$$

Values of k$_{obs}$ were obtained from the ln(C$_\infty$ − C$_t$) *vs.* time plots. The solutions were prepared by dissolving the precursor (1.0 × 10^{-3} mol L^{-1}) in dichloromethane containing 0.1 mol L^{-1} tbap and then adding the N-heterocyclic ligand L (concentration of 2.0; 5.0; 10.0; 15.0; 20.0 and 40.0 × 10^{-3} mol L^{-1}).

Thermodynamic parameters were determined by inserting data in the Arrhenius and Eyring equations.[17,18] For this purpose, the experiments were carried out at 5 °C steps in the temperature range of 5 to 25 °C.

X-ray crystallography

Crystals of [RuCl(4-vnpy)(P-P)(bipy)]PF$_6$ were grown by slow evaporation of a dichloromethane/diethyl ether solution. The crystals were mounted on an Enraf-Nonius Kappa-CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ (λ = 0.71073 Å) radiation. The final unit-cell parameters

were based on all reflections. Data were collected with the COLLECT program;[19] integration and scaling of the reflections were performed with the HKL DENZO-SCALEPACK software package.[20] Absorption correction was carried out by the Gaussian method.[21] The structure was determined by direct methods with SHELXS-97.[22] The model was refined by full-matrix least squares on F^2 by means of SHELXL-97.[23] All hydrogen atoms were stereochemically positioned and refined with a riding model. The ORTEP view shown in Figure 1 was prepared with ORTEP-3 for Windows.[24] Hydrogen atoms on the aromatic rings were refined isotropically, each one with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the atom to which it was bonded. The data collection and experimental details are summarized in Table 1, and the selected bond distances and angles are given in Table 2.

Table 1. Details of the X-ray diffraction experiment and lattice parameters determined for [RuCl(4-vnpy)(P-P)(bipy)]PF₆·0.3 CH₂Cl₂

Empirical formula	$C_{45}H_{43}ClF_6N_3P_3Ru \cdot 0.3CH_2Cl_2$
Formula weight	994.73
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 0.5990(1)$ Å
	$b = 14.7103(2)$ Å
	$c = 15.0518(2)$ Å
	$\alpha = 79.234(1)°$
	$\beta = 77.421(2)°$
	$\gamma = 79.457(1)°$
Volume (Å³)	2225.63(5) Å³
Z	2
Density (calculated)	1.484 g cm⁻³
Absorption coefficient	0.617 mm⁻¹
F(000)	1013
Reflections collected	14815
Independent reflections	7826 [R(int) = 0.0175]
Completeness to theta = 25.00°	99.6%
Absorption correction	Semi-empirical from equivalents
Final R indices [I>2sigma(I)]	$R_1 = 0.0409$, $wR_2 = 0.1140$
R indices (all data)	$R_1 = 0.0465$, $wR_2 = 0.1200$

Theoretical calculations

The geometry optimization was performed with the Spartan 06 package, employing the B3LYP hybrid density functional combined with the 6-31G* basis sets and LACVP* for Ru atoms.[25-28] A PC with an Intel Dual Core processor (3.0 GHz), 4 GB of RAM memory and 160 GB of hard disk space was used for the these calculations.

Synthesis of [RuCl(4-vnpy)(P-P)(bipy)]PF₆

The [RuCl(4-vnpy)(P-P)(bipy)]PF₆ complex was synthesized from 0.050 g (0.066 mmol) of the *cis*-[RuCl₂(P-P)(bipy)] precursor, dissolved in 3 mL dichloromethane with 0.043 mL (0.398 mmol) of 4-vinylpyridine. This mixture was stirred at room temperature for 3 h, and 43.19 mg (0.265 mmol) of NH₄PF₆, dissolved in methanol, were then added. After 30 min of stirring, the volume of the reaction was reduced to *ca.* 1 mL, and hexane was added to precipitate the complex, which was filtered off, thoroughly washed with H₂O and ether and dried under vacuum. Yield: 89%. Anal. calc. for $C_{45}H_{43}ClF_6N_3P_3Ru$: C, 55.76; N, 4.34; H, 4.47%. Found: C, 55.66; N, 4.32; H, 4.67%. ³¹P{¹H} NMR, in CH₂Cl₂, 20 °C: δ 37.77; 37.06 (doublets, $^2J_{P-P}$ 34.00 Hz).

Results and Discussion

The reactions of the precursors *cis*-[RuCl₂(P-P)(N-N)] with the monodentate ligands L = 4-methylpyridine, 4-phenylpyridine, pyridine and 4-vinylpyridine produce complexes whose general formula is [RuCl(L)(P-P)(N-N)]⁺, as shown in Scheme 1.

The proximity of the doublets in the ³¹P{¹H} NMR spectra of the complexes in the series [RuCl(L)(P-P)(N-N)]PF₆ (N-N = 2,2′-bipyridine and L = 4-methylpyridine, 4-phenylpyridine, pyridine and vinylpyridine), Δσ < 1, is consistent with both phosphorus atoms being positioned *trans* to the nitrogen atoms. This suggests that the chloride dissociated from the precursors, in this series, is always the one that is *trans* to a phosphorus atom. This is confirmed by the X-ray structures of the complexes.[7,29,30]

The X-ray structures of [RuCl(4-pic)(P-P)(bipy)]PF₆, [RuCl(Phpy)(P-P)(bipy)]PF₆ and [RuCl(py)(P-P)(bipy)]PF₆ have been published previously.[7,29-31] In this work, we report the structure of [RuCl(4-vnpy)(P-P)(bipy)]PF₆ (Figure 1).

The X-ray structural analysis of the complex [RuCl(4-vnpy)(P-P)(bipy)]PF₆ shows that the chloride is *trans* to one of the 2,2′-bipyridine nitrogens (N1) and the 4-vinylpyridine
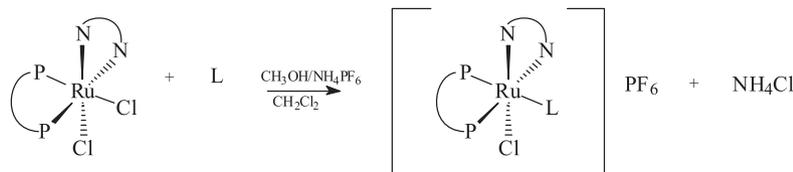
Scheme 1. Kinetics of dissociation of a chloride from *cis*-[RuCl₂(P-P)(N-N)]PF₆ complexes (L = pyridine or 4-metylpyridine).
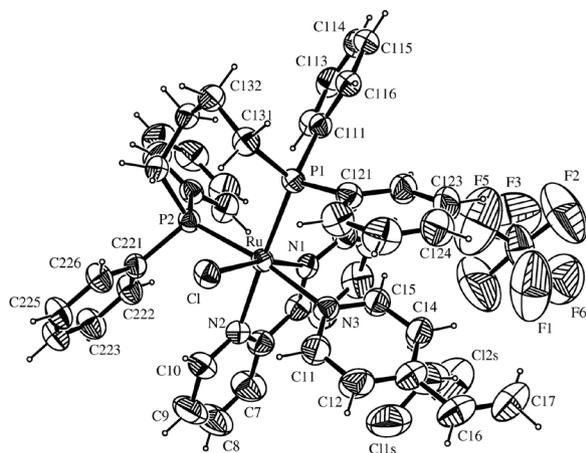
Figure 1. ORTEP drawing of [RuCl(4-vnpy)(P-P)(bipy)]PF$_6$ with 50% probability ellipsoids.

Table 2. Selected bond lengths (Å) and angles (°) for [RuCl(4-vnpy)-(P-P)(bipy)]PF$_6$

Bond lengths	(Å)	Angles	(°)
Ru-N(3)	2.207(3)	Cl-Ru-N(3)	88.6(7)
Ru-N(2)	2.125(3)	Cl-Ru-P(2)	85.3(3)
Ru-N(1)	2.083(3)	Cl-Ru-N(2)	92.2(8)
Ru-P(2)	2.3290(8)	Cl-Ru-P(1)	86.8(3)
Ru-P(1)	2.3573(8)	P(2)-Ru-N(1)	100.8(7)
Ru-Cl	2.4256(8)	P(2)-Ru-N(2)	89.9(8)

is *trans* to one of the phosphorus atoms (P2). The Ru-N(3) (2.207(3) Å) distance is longer than the Ru-N(2) bond (2.125(3) Å), as expected, since the 4-vinylpyridine is a monodentate ligand, while the 2,2´-bipyridine is bidentate. In this case, the bidentate ligand is more tightly bonded to the metal center. On the other hand, the distance Ru-P(1) (2.3573(8) Å), Ru-P(1) *trans* to N(2), is longer than the distance Ru-P(2) (2.3290(8) Å), Ru-P(2) *trans* to N(3), since the 2,2´-bipyridine affects the P-Ru bonds *trans* to it more effectively than does the monodentate 4-vinylpyridine ligand. The bond distances and angles listed in Table 2 are in the range expected for ruthenium diphosphine complexes.[7,12-14,29-32] Similar behavior was observed for the complexes containing 4-methylpyridine and 4-phenylpyridine, as previously reported.[7,29,30] In all three complexes, the dissociated chloride was always the one *trans* to a phosphorus atom in the precursor *cis*-[RuCl$_2$(P-P) (bipy)], as expected, given the stronger *trans* effect of the phosphorus atom and in accordance with the X-ray structures.

The electrochemical data for the *cis*-[RuCl$_2$(P-P)(N-N)] complexes, obtained by cyclic voltammetry, are shown in Table 3.

Typical differential pulse voltammograms recorded during the kinetic experiments can be seen in Figure 2, which

Table 3. Electrochemical parameters for *cis*-[RuCl$_2$(P-P)(N-N)] complexes[a]

Complex	E$_{1/2}$ / mV	E$_{pa}$ / mV	E$_{pc}$ / mV	pK$_a$
cis-[RuCl$_2$(P-P)(Cl-bipy)]	733	781	685	2.61
cis-[RuCl$_2$(P-P)(bipy)]	592	665	518	4.44
cis-[RuCl$_2$(P-P)(Me-bipy)]	585	668	501	4.92
cis-[RuCl$_2$(P-P)(MeO-bipy)]	546	586	505	5.74

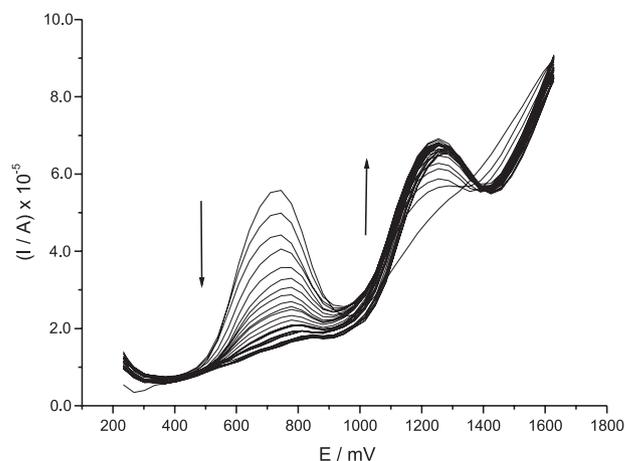[a] Pt electrode *vs.* Ag/AgCl, in CH$_2$Cl$_2$; ferrocene was used as reference.

Figure 2. Differential pulse voltammograms of the mixture of *cis*-[RuCl$_2$(P-P)(Cl-bipy)] with pyridine in CH$_2$Cl$_2$. Experimental conditions: 0.1 mol L^{-1} tbap, 20 °C, 1/10 complex/ligand, Pt *vs.* Ag/AgCl. Sweep rate: 170 mV s^{-1}.

shows the consumption of the precursor (E$_{ap}$ *ca.* 700 mV) and appearance of the product of the reaction (E$_{ap}$ *ca.* 1.200 mV) over time.

The plot of k$_{obs}$ *vs.* [py] (Figure 3) gives the dissociation constant of one chloride from the coordination sphere of the ruthenium center. The values for all four complexes tested in this experiment are shown in Table 4.
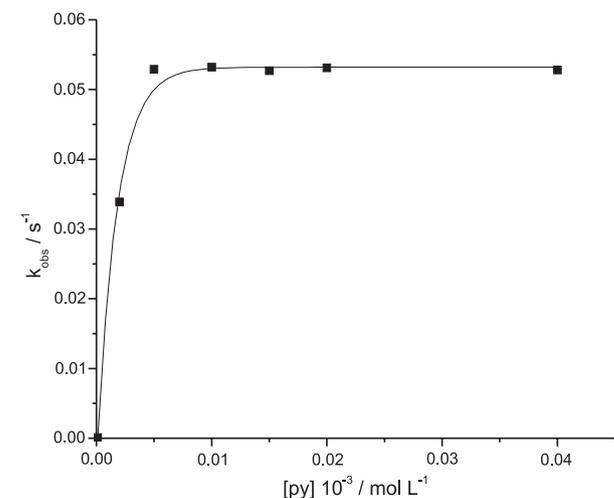

Figure 3. Plot of k$_{obs}$ *vs.* [py] for the formation of [RuCl(py)(P-P)(bipy)]$^+$ in CH$_2$Cl$_2$. [Ru] = 1.0 × 10^{-3} mol L^{-1}; T = 20 °C; [tbap] = 0.1 mol L^{-1}.

Table 4. Values of k_f (s⁻¹) for the formation of [RuCl(L)(P-P)(N-N)]⁺ complexes (L = py and 4-pic)

N-N	Cl-bipy		bipy		Me-bipy		MeO-bipy	
				[RuCl(L)(P-P)(N-N)]⁺ k_f / s⁻¹ (error)				
L	py	4-pic	py	4-pic	py	4-pic	py	4-pic
	1.07×10^{-2} (0.0002)	1.03×10^{-2} (0.0002)	5.30×10^{-2} (0.0008)	5.06×10^{-2} (0.0006)	6.60×10^{-2} (0.0023)	7.01×10^{-2} (0.0055)	8.89×10^{-2} (0.0052)	8.70×10^{-2} (0.0085)

Figures 4A and 4B show the inverse linear relationship between the k_{diss} values obtained for the *cis*-[RuCl₂(P-P)(N-N)] complexes and their oxidation and half-wave potentials [calculated from $(E_1 + E_2)/2$], while Figures 5A and 5B show the linear relationship between the k_{diss} of the complexes and the percentage of contribution of the Ru d-orbitals to the electron density in the HOMO.

As can be seen in Figures 4 and 5, there is a good correlation between the values plotted for the substitution of the chloride by the pyridine ligand, suggesting that the higher the electron density of the metal center, the easier is the dissociation of the chloride from the coordination sphere of the complex. As can be observed from the plots in Figure 5, although the difference in the percentages of Ru(d) contribution to the HOMOs of the complexes is quite small, k_{diss} increases linearly as the percentage of Ru(d) in the HOMO increases. It is worth pointing out that there is a better correlation between k_{diss} and the electron density
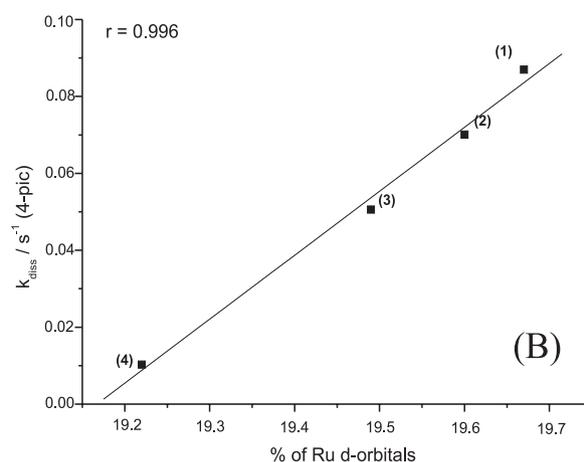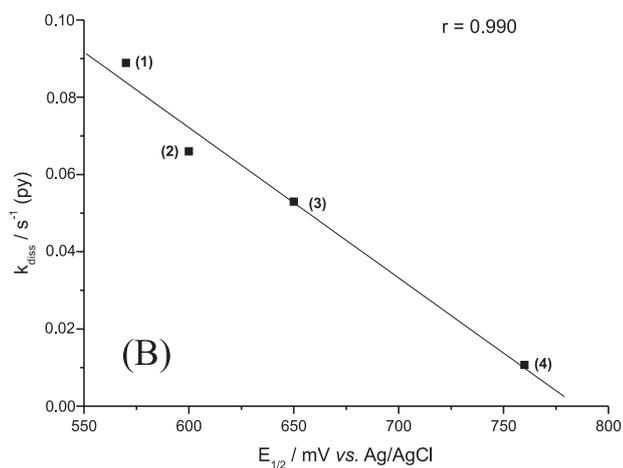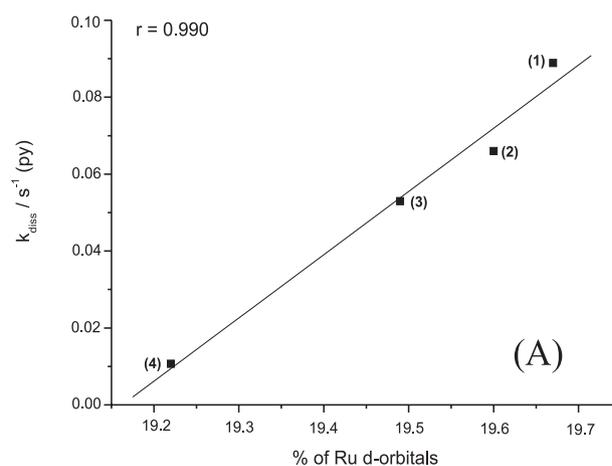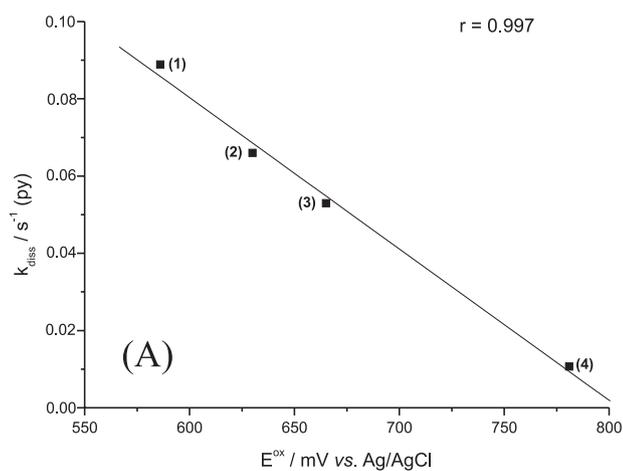

Figure 4. Relationship between the k_{diss} values of the chloride replaced by pyridine and (A) oxidation potentials (E_{ox}) and (B) half-wave potentials ($E_{1/2}$) of the complexes: (1) *cis*-[RuCl₂(P-P)(MeO-bipy)]; (2) *cis*-[RuCl₂(P-P)(Me-bipy)]; (3) *cis*-[RuCl₂(P-P)(bipy)] and (4) *cis*-[RuCl₂(P-P)(Cl-bipy)

Figure 5. Relationship between the percentage of participation of the Ru d-orbitals in the HOMO of the complexes and the k_{diss} of the chloride replaced by (A) pyridine and (B) 4-methylpyridine in: (1) *cis*-[RuCl₂(P-P)(MeO-bipy)], (2) *cis*-[RuCl₂(P-P)(Me-bipy)], (3) *cis*-[RuCl₂(P-P)(bipy)] and (4) *cis*-[RuCl₂(P-P)(Cl-bipy)].

contribution from the Ru d-orbitals to the HOMO than between k_{diss} and the electron density in the metal center as a whole (not shown). Thus, it may be concluded from the DFT calculations that the main metal electron density contribution to the HOMO, a frontier orbital of the complex, comes from the ruthenium d level and not from its inner levels.[7-11] Moreover, as can be seen in Tables 3 and 5, the higher the percentage of the electron density of the Ru d-orbital in the HOMO, as calculated by the DFT method, the lower are the oxidation potentials of the metal center in the complexes.

Figure 6 shows a graphic representation of the HOMO and LUMO of the *cis*-[RuCl$_2$(P-P)(bipy)] complex under study and Table 5 lists the electron density contributions of selected atoms to the HOMO of the complexes.
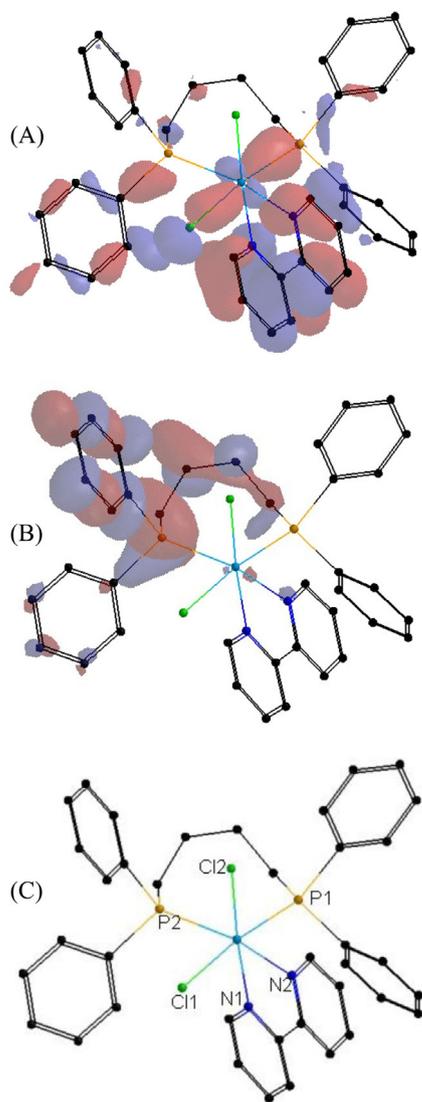

Figure 6. Graphic representation of the A) HOMO, B) LUMO and C) molecular model of the complex *cis*-[RuCl$_2$(P-P)(bipy)] (online version in color).

Table 5. Percentages of contribution of selected atoms to the HOMO of *cis*-[RuCl$_2$(P-P)(N-N)] complexes

X-bipy	MeO-bipy	Me-bipy	bipy	Cl-bipy
Ru (d)	19.67	19.60	19.47	19.22
Ru	22.46	22.51	22.95	22.05
Cl1 (Cl1-Ru-P1)	13.41	13.51	14.13	13.89
Cl2 (Cl2-Ru-N1)	9.56	9.69	10.05	9.83
N1 (N1-Ru-Cl2)	1.77	1.80	1.81	1.84
N2 (N2-Ru-P2)	1.07	1.15	1.19	1.19
P1 (P1-Ru-Cl1)	4.21	4.43	4.38	4.22
P2 (P2-Ru-N2)	1.23	1.27	1.28	1.25

As can be seen in Table 5, in all four complexes the chloride *trans* to the phosphorus atom (Cl1) contributes more electron density to the HOMO of the compound than the chloride (Cl2) *trans* to the nitrogen atom. It is likely that this is a consequence of the stronger *trans* effect exerted by the phosphorus atoms than by the nitrogen atoms. Because of this, the Ru-Cl bond distances in the *cis*-[RuCl$_2$(P-P)(N-N)] complexes for the chloride *trans* to the phosphorus atoms are always longer than those for chlorides *trans* to the nitrogen atoms of X-bipy ligands.[31] It can also be seen from Table 5 that the HOMO electron densities on the two chlorides of each complex are different, allowing them to be dissociated selectively. Accordingly, the chloride *trans* to the phosphorus atom should be more labile, which was confirmed experimentally. Thus, in the reactions of the *cis*-[RuCl$_2$(P-P)(N-N)] complexes with N-heterocyclic ligands, the substituted chloride is always the one that is *trans* to the phosphorus atom, as seen in the X-ray structures of the [RuCl(L)(P-P)(N-N)]PF$_6$ (L= 4-pic, 4-Phpy, py, 4-vnpy) complexes.[7,29,30] The data in Table 5 show that the Ru d-orbital contributes more effectively to the HOMO of the complexes in the order: MeO-bipy > Me-bipy > H-bipy > Cl-bipy. This is the same order as that of the dissociation rates of the substitution reactions of the *cis*-[RuCl$_2$(P-P)(N-N)] complexes with the N-heterocyclic ligands and also the same order as that of increasing half-wave oxidation potentials of the metal center (Tables 3 and 4). All these data lead to the conclusion that the rate of substitution reactions in the *cis*-[RuCl$_2$(P-P)(N-N)] complexes increases with the electron density from Ru(d) located in the HOMO of the complex, and this electron density is expressed experimentally by the oxidation potential of the metal center in the compound.

The rate constant for the dissociation of the chloride from the coordination sphere of the metal center in [RuCl(NH$_3$)$_5$]$^+$ is 4.4 s^{-1} at 20 °C, higher than for the analogous dissociation in the *cis*-[RuCl$_2$(P-P)(N-N)] species.[32] This can be explained by the fact that in [RuCl(NH$_3$)$_5$]$^+$ there are only σ-donor ligands, making the

Table 6. Thermodynamic activation parameters for the formation of [RuCl(py)(P-P)(N-N)]PF$_6$ complexes

Activation parameters	Cl-bipy	bipy	Me-bipy	MeO-bipy
$E_a{}^a$	50.91 (± 7.61)	43.30 (± 4.31)	38.58 (± 4.35)	33.81 (± 2.72)
$\Delta G^{\#a}$	83.17	79.83	79.78	78.07
$\Delta H^{\#a}$	48.45 (± 7.45)	42.13 (± 4.77)	36.07 (± 4.52)	31.67 (± 2.76)
$\Delta S^{\#b}$	−116.56 (± 25.56)	−126.57 (± 17.45)	−146.77 (± 15.89)	−155.64 (± 9.62)

^{a} kJ mol^{-1}; ^{b} J mol^{-1} K^{-1}.

Table 7. Thermodynamic activation parameters for the formation of [RuCl(pic)(P-P)(N-N)]PF$_6$ complexes

Activation parameters	Cl-bipy	bipy	Me-bipy	MeO-bipy
$E_a{}^a$	54.47 (± 7.82)	43.72 (± 4.18)	37.74 (± 5.10)	35.43 (± 5.31)
$\Delta G^{\#a}$	82.72	79.99	79.58	78.19
$\Delta H^{\#a}$	52.59 (± 8.03)	41.29 (± 3.89)	35.39 (± 5.10)	33.18 (± 5.48)
$\Delta S^{\#b}$	−101.17 (± 27.65)	−129.91 (± 13.30)	−148.24 (± 17.82)	−151.00 (± 19.24)

^{a} kJ mol^{-1}; ^{b} J mol^{-1} K^{-1}.

ruthenium softer, the Ru-Cl bond weaker and the chloride easier to be dissociated from the metal center. The k_{diss} values reported here are also lower than those obtained for the *trans*-[Ru(NH$_3$)$_4$(PPh$_3$)(H$_2$O)]$^{2+}$ complexes, for which the value 3.9 L mol^{-1} s^{-1} was found.[33]

The thermodynamic parameters for the reactions, calculated with the Arrhenius and Eyring equations,[17,18] are given in Tables 6 and 7.

Again, it is seen that the rate constants for chloride substitution in the *cis*-[RuCl$_2$(P-P)(N-N)] compounds increase in the same order as that for decreasing activation energies and enthalpies, suggesting that, indeed, the breaking of the Ru-Cl bond in the complexes is the rate-determining step of these reactions. It should be mentioned that $\Delta S^{\#}$ for a dissociation mechanism should be positive; however, in the present reactions these values were negative. Certainly, the reason for this is that in these processes charged species were produced during the substitution reactions from the uncharged *cis*-[RuCl$_2$(P-P)(N-N)] precursors.

Conclusions

The *trans* effect has long been recognized as a strong driving force for ligand substitution reactions in coordination complexes. It can exert a great influence upon the metal-to-ligand bonding and the lability of ligands within a complex. This effect was observed clearly in the dissociation reactions of *cis*-[RuCl$_2$(P-P)(N-N)] complexes, in that only the chloride *trans* to the phosphorus atom of the 1,4-bis(diphenylphosphino)butane ligand was dissociated, even in the presence of an excess of the entering ligands, forming the *cis*-[RuCl(L)(P-P)(N-N)]PF$_6$

(L = N-heterocyclic monodentate ligand) products. The easier dissociation of the chloride *trans* to the phosphorus atom is consistent with the results of DFT calculations, which show that the contribution of the electron density of the chloride to the HOMO is higher when the Cl$^-$ ligand is *trans* to the phosphorus atom than when it is *trans* to the nitrogen atom in the *cis*-[RuCl$_2$(P-P)(N-N)] complexes. Thus, the DFT calculations can be a useful tool, aiding the understanding of the reactivity of coordination compounds.

The $\Delta H^{\#}$ values of the dissociation reactions of the *cis*-[RuCl$_2$(P-P)(N-N)] complexes are close to 40.0 kJ mol^{-1} and show a tendency to decrease with the increase in the pK$_a$ of the N-N ligands. The negative $\Delta S^{\#}$ values of these reactions are probably due to the charge generated in the [RuCl(L)(P-P)(N-N)]$^+$ products.

Acknowledgments

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